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Non-Thermal Plasma Activated deNO_x Catalysis

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Abstract

The combination of non-thermal plasma (NTP) with catalyst systems as an alternative technology to remove NO_x emissions in the exhaust of lean-burn stationary and mobile sources is reviewed. Several factors such as low exhaust gas temperatures (< 300 °C), low selectivity to N₂ and the presence of impurities make current thermally activated technologies inefficient. Various plasma-catalyst systems have been examined and shown to have a synergistic effect on the de-NO_x efficiency when compared with NTP or catalyst alone systems. The NTP is believed to form oxygenated species such as aldehydes, nitrogen-containing organic species and convert NO to NO₂, which improves the reduction efficiency to N₂ during hydrocarbon-selective catalytic reduction reactions. The NTP has been used as a pretreatment to convert NO to its higher oxidation states such as NO₂ to improve NO_x reduction efficiency in the subsequent processes e.g. NH₃-selective catalytic reduction. It has been applied to the lean phase of the NO_x storage to improve the adsorption capacity of the catalyst by conversion of NO to NO₂. Alternatively, a catalyst with high adsorption capacity is chosen and the NTP is applied to the rich phase to improve the reduction activity of the catalyst at low temperature.

Keywords: Catalyst, Plasma, NO_x removal, SCR, NSR

1. Introduction

The treatment of the high levels of NO_x emissions in lean-burn automotive engines exhaust is a challenge. While several gas after-treatments systems have been reported [1–3], in all cases the issues of low temperature activity, selectivity to N_2 and resistance to impurities in the exhaust gas feed, for example SO_x , are problematic. In an attempt at addressing such issues, alternative approaches such as hybrid non-thermal plasma (NTP)-catalyst systems have been explored. In these systems, the effect of the plasma can be related to:

- Gas heating (Joule effect) by vibrational excitation and dissociation of molecules, which proceed much faster than in any conventional heat exchanger due to electronic and ionic collision [4].
- Electronic excitation of molecules
- Formation of short lived radicals. In the case of diesel and lean-burn engines atomic (N), excited nitrogen (N_2^*), electronically excited oxygen ($\text{O}(^1\text{D})$) (due to high reactivity) may be formed [5]
- Formation of long lived intermediate species (100 μs): ground state atomic oxygen (O), hydroxyl (OH), peroxy radicals (R-OO) [6]
- UV emission
- Surface modification of the catalyst.

The present review compares the various hybrid NTP-catalyst approaches that have been reported for the removal of NO_x . In these hybrid systems, the reactor configuration can be very important and two main configurations are used namely the 'In Plasma Configuration' (IPC) and the Post-Plasma Configuration (PPC). The IPC involves placing the catalyst in the discharge area since this potentially allows making use of the short lived intermediates created by the plasma for reaction on the catalyst surface. In the PPC, the catalyst is placed downstream of the plasma and in this case the lifetime of

the intermediates formed by the plasma must be sufficiently long to influence the reaction on the catalyst surface [4]. These configurations are shown in [Figure 1](#).

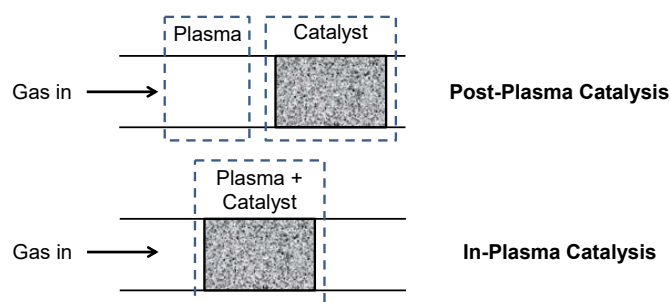


Figure 1. Two main reactor configurations are used in the hybrid plasma-catalyst systems.

2. Hydrocarbon-selective catalytic reduction (HC-SCR) using NTP

Pan *et al.* [7] reported a synergistic effect of the NTP on NO_x reduction by CH_4 over an In/H-BEA catalyst using a post-plasma hybrid system (*i.e.* an enhancement in de- NO_x efficiency using PPC system compared to NTP or catalyst system alone). A gas mixture containing 540 ppmv NO, 60 ppmv NO_2 , 600 ppmv CH_4 , O_2 with a balance of Ar was introduced to the system while varying the plasma energy density and temperature. A significant promotion effect on NO_x removal by the hybrid system was observed at 250–550 °C. Further increases in temperature had a detrimental effect on the NO_x removal *i.e.* an increase in plasma energy density from 0 to 135 J L^{-1} increased the NO_x removal below 550 °C while higher temperatures decreased the NO_x removal. The T_{50} , *i.e.* temperature at 50% NO_x conversion, decreased from above 380 °C at 0 J L^{-1} (no NTP present) to $\sim 325 \text{ °C}$ at 135 J L^{-1} , revealing higher efficiency of the hybrid system at low temperatures. The promoting effect of the NTP on CH_4 -SCR was studied by product analysis after the NTP-alone. In the low temperature region, it was attributed to the NO oxidation and CH_4 conversion into helpful intermediates such as HCHO, CH_3NO and CH_3NO_2 . However, at high temperatures, the combustion of the intermediates with O_2 became the dominant reaction and decreased the NO_x removal efficiency. Introduction of CH_4

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seperately to SCR and DBD reactors at different ratios in order to widen the operational temperature was also examined. A wide temperature window was observed when 400 ppmv and 200 ppmv CH₄ was injected to the DBD and SCR reactors, respectively [7]. The removal of NO and CH₄ using a PPC system over Cu-based catalysts on different supports has also been reported. A plasma with an energy density of 1800 J L⁻¹ was shown to promote the NO and CH₄ removal within 25-500 °C. NO removal efficiency was also significantly affected by the type of catalyst support and decreased in the following order: CuO/CeO₂/TiO₂/γ-Al₂O₃ > CuO/TiO₂/γ-Al₂O₃ > CuO/γ-Al₂O₃ > CuO/TiO₂. The characterization results indicated that CuO/CeO₂/TiO₂/γ-Al₂O₃ catalyst, with respect to other catalysts, had larger amount of Cu²⁺ incorporated within CeO₂ and TiO₂ species which could possibly be correlated to its relative higher catalytic activity [8].

Rajanikanth *et al.* reported a series of studies examining the deNO_x efficiency of a stationary 4.4 kW diesel engine exhaust at no load and 50% load conditions, using NTP-catalyst or adsorbent processes [9–13]. The filtered exhaust before the aftertreatment system included NO, NO₂, CO, hydrocarbons, aldehydes and CO₂. Using a two-stage plasma-activated alumina catalyst system, without the addition of any reductant, it was shown that this process exhibited an enhancement in de-NO_x efficiency. The plasma reactor (75 J L⁻¹) was operated at room temperature, while the catalyst reactor was operated at 300 °C. 57% de-NO_x removal was achieved using two-stage system, compared with the 20% and 22% with separate catalyst or plasma processes, respectively. The improvement in the de-NO_x efficiency was more pronounced when the plasma reactor was operated at 150 °C. The NO_x removal efficiency using the plasma-only process was ~5% while increased to ~50% using the two-stage process. The plasma was believed to convert NO to NO₂ efficiently, given the lean condition of the exhaust and also convert hydrocarbons to aldehydes, which reacted above 250 °C over activated alumina, forming N₂ and resulting in an increase in NO_x removal efficiency [10,13]. To achieve higher conversions, a four-stage process (plasma-catalyst-plasma-catalyst) was also examined and at constant energy density, the four-stage process showed an even better performance, compared with the two-stage process, in terms of NO_x removal [10]. However, the four-stage process makes the design of aftertreatment system complicated. The temperature variation in the catalyst reactor, while

operating the plasma reactor (52 J L^{-1}) at room temperature, was also reported. An increase in the temperature of the catalyst reactor from 25 to 250 °C led to a gradual decrease in the de- NO_x results from ~55% to ~40%, respectively, which was thought to be due to a decrease in the adsorption of the activated alumina, and then, increased to 57% at 300 °C. The activated alumina was believed to not be catalytically active below ~300 °C and acted as an adsorbent at low temperatures [10].

Combining low and high temperature-active catalytic materials has been shown to enhance the temperature range during post plasma-SCR of NO_x [14]. Ba/zeolite Y and Ag/ $\gamma\text{-Al}_2\text{O}_3$ catalysts were combined in different configurations e.g. dual bed, mixed bed or separately, and examined in the post plasma-SCR of a simulated exhaust gas feed between 100-500 °C under steady-state and transient operation. Steady-state experiments were performed at 200, 350 and 500 °C with both the plasma and SCR reactors held at the same temperature, while transient experiments were performed by heating and cooling the plasma and SCR reactors with each heating or cooling defined as one thermal cycle. The latter process was conducted at $10 \text{ }^\circ\text{C min}^{-1}$ between 100-500 °C after holding for 12 min at the minimum or maximum temperature, respectively. This thermal cycling was continued until the last two consecutive cycles overlapped. The best configuration to reduce NO_x levels in the exhaust was found for the Ba/zeolite Y catalyst placed before the Ag/ $\gamma\text{-Al}_2\text{O}_3$ catalyst. The higher activity of this configuration was attributed to the formation of formaldehyde over the Ba/zeolite Y catalyst which then acted as a reductant over the Ag/ $\gamma\text{-Al}_2\text{O}_3$ catalyst. On adding propene as a reductant at a $\text{C}_1:\text{NO}_x = 12$, resulted in steady-state NO_x conversion above 80% at 200 °C and 95% at 500 °C while the average NO_x conversion under transient operation between 100 °C and 500 °C was around 70%. In the latter case, the drop in NO_x conversion was thought to be due to the desorption of NO_x at temperatures below 200 °C and the low activity of the Ag/ $\gamma\text{-Al}_2\text{O}_3$ catalyst at these temperatures [14].

Cho *et al.* [15] reported a post-plasma SCR system applied to the exhaust of a 4.9L, 6 cylinder Isuzu diesel engine dynamometer system specifically at low temperatures. In this system, oxygenated hydrocarbons were generated by reforming the diesel fuel through an air plasma reactor. The plasma-induced air and highly active oxygenated hydrocarbons were added to a sidestream of the exhaust of

the Isuzu diesel engine prior to the SCR system. The plasma air containing O_3 , a stronger oxidizing agent compared to O_2 , was believed to convert the NO to NO_2 and partially oxidize hydrocarbons which then increase the NO_x conversion in the SCR reactor. The experiments were performed under steady-state FTP simulated conditions that provided an actual vehicle certification test, despite of the exclusion of cold start and transient operation conditions (the exhaust temperature varied from 150 to 500 °C). Dual-bed catalysts such as Ba/zeolite Y-Cu/zeolite Y and Ba/zeolite Y-Ag/ Al_2O_3 were tested as SCR catalysts with the Ba/zeolite Y-Cu/zeolite Y catalysts, showing the best performances (~60% mode-averaged NO_x conversion). This was attributed to the higher oxidation activity of the Cu catalysts compared to the Ag ones due to inhibition of the latter by heavy HCs present in the exhaust at temperatures < 300 °C [15].

Peng *et al.* [16] observed a synergistic effect between the catalyst and the plasma in the NO_x removal over a perovskite catalyst ($La_{0.8}K_{0.2}Cu_{0.05}Mn_{0.95}O_3$). A mixture of NO, O_2 and C_3H_6 was passed through a plasma DBD reactor filled with $\gamma-Al_2O_3$ powder before passing over a catalyst bed mixed with soot, with the latter being heated from 100 to 500 °C. The results showed a maximum NO_x removal rate of 44% with plasma-alone, compared with 72% with the plasma-catalyst system when using 0.27% C_3H_6 in the feed. Lee *et al.* [17] also reported an improvement in the catalyst activity during C_3H_6 -SCR, when using a plasma DBD reactor to pre-treat the feed containing 1660/23 ppm NO/ NO_2 , 1800 ppm C_3H_6 (hydrocarbon (C_1 -based)/ NO_x ratio = 3.2), 10% O_2 , He or N_2 balance at < 400°C in a PPC system. Using this system, the NO_x to N_2 conversion was 40 – 50% with a Ag/ Al_2O_3 catalyst at 300-500 °C, revealing a better performance compared to $\gamma-Al_2O_3$ as the catalyst. The results with N_2 balance and He balance were found to be identical when the NO/ NO_2 ratio remained constant after the DBD reactor, although this led to a significant difference in the energy densities used (10 J L⁻¹ when using a He as balance compared with 36 J L⁻¹ with the N_2). The plasma was believed to oxidize a portion of NO in the feed to NO_2 under lean-burn conditions which facilitated the NO_x conversion to N_2 under HC-SCR conditions. The presence of hydrocarbons in the feed was believed to promote NO oxidation and form nitrogen-contained organic compounds that further reacted on the catalyst to form N_2 and CO_x .

The mechanism of NO_x removal using a post plasma-SCR system has been examined by considering the long-lived chemical products generated in the plasma [18]. The SCR reaction alone over a Ag/Al₂O₃ catalyst (using a feed mixture of 435 ppm NO, 10 ppm NO₂, 6000 ppm C₂H₄, 8% O₂ and balance N₂) indicated that temperatures higher than 300 °C were needed to activate the catalyst and obtain high NO_x conversions. For example, the thermal NO_x removal efficiency at 240 °C was only 6.7%. Treatment of the feed with plasma before the SCR reaction at 240 °C resulted in an increase in the NO_x removal efficiency to 90.1%, revealing the synergistic effect in the post plasma-SCR system. Analysis of the products obtained after the plasma treatment (703 J L⁻¹) showed that of all NO was converted. A portion was converted to NO₂ and, due to the presence of hydrocarbons, some was also converted to nitrogen-contained organic compounds such as methyl nitrate (CH₃NO₂), nitro methyl (CH₃CN) and ethyl nitrate (C₂H₅ONO₂), as postulated by Nie *et al.* [18]. Post plasma product analysis also revealed the presence of other organic compounds such as formaldehyde (HCHO), acetaldehyde (CH₃CHO) and acetylene (C₂H₂).

Gas phase plasma treatments can lead to many reaction intermediates. A proposed reaction mechanism during gas phase plasma of NO/NO₂/C₂H₄/O₂/N₂ feed system based on product analysis and previous studies is summarised in [Table 1](#) [18]. It is believed that radicals predominantly participated in the reaction during gas phase plasma [17]. The gas phase plasma in the presence of hydrocarbons under the lean conditions is effective in oxidizing the NO to NO₂. For example, considering the aforementioned feed system, oxidative species via reactions R11-R16, including CH₃O₂, C₂H₅O₂, O₃ and HO₂ can oxidize NO to NO₂ via reactions R18-R21. NO_x removal in this feed system can then occur through different routes. The dissociation energy of O₂ (R1; 5.1 eV) is much smaller than N₂ (R2; 9.8 eV) [17] and this leads to the formation of more O radicals and thus, oxidative species rather than N radicals under the lean conditions of the exhaust. The low concentration of N radicals accounts for small NO_x conversion to N₂ and N₂O in excess oxygen via reactions R34 and R35. The NO_x removal via OH radicals to form HNO₂ and HNO₃ (reactions R36 and R37) are also considered negligible due to the absence of H₂O in the feed and consequent small

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concentrations of OH radicals although this mechanism cannot be ignored in the real automotive exhaust gas feed due to high H₂O concentrations. It is likely that the NO_x removal predominantly occurs via the formation of nitrogen-contain organic chemicals such as CH₃ONO₂, C₂H₅ONO₂ and CH₃NO₃ in this system [11,18]. O radicals at high concentration in the plasma decompose C₂H₄ via reactions R3-R6 and form oxygenated byproducts such as CO, CO₂, HCHO and C₂H₃. After the two-stage plasma-SCR process, all the organic compounds formed during the plasma treatment are removed and NO_x removal efficiency increases. The aldehydes, NO₂ and nitrogen-containing organic hydrocarbons formed in the gas phase plasma are more active in the SCR over Ag/Al₂O₃ catalyst than, for example, C₂H₄ and their formation thus increases the NO_x conversion to N₂ [18].

Table 1. Proposed reaction mechanism during gas phase plasma treatment of NO/NO₂/C₂H₄/O₂/N₂ system. Adapted from [18].

Reaction	Number
$e + O_2 \rightarrow e + O + O$	R1
$e + N_2 \rightarrow e + N + N$	R2
$C_2H_4 + O \rightarrow CH_2COH + H$	R3
$C_2H_4 + O \rightarrow CH_3 + HCO$	R4
$C_2H_4 + O \rightarrow HCHO + CH_2$	R5
$C_2H_4 + O \rightarrow C_2H_3 + OH$	R6
$C_2H_4 + H \rightarrow C_2H_5$	R7
$C_2H_4 + HO_2 \rightarrow CH_3CHO + OH$	R8
$C_2H_4 + OH \rightarrow C_2H_3 + H_2O$	R9
$C_2H_4 + OH \rightarrow HCHO + CH_3$	R10
$CH_3 + O_2 \rightarrow CH_3O_2$	R11
$O_2 + C_2H_5 \rightarrow C_2H_5O_2$	R12
$H + O_2 + M \rightarrow HO_2 + M$	R13
$O + O_2 + M \rightarrow O_3 + M$	R14
$HCO + O_2 \rightarrow CO + HO_2$	R15
$CH_2COH + O_2 \rightarrow H_2C=C=O + HO_2$	R16
$H_2C=C=O + H \rightarrow CO + CH_3$	R17
$CH_3O_2 + NO \rightarrow CH_3O + NO_2$	R18
$O_3 + NO \rightarrow O_2 + NO_2$	R19
$HO_2 + NO \rightarrow OH + NO_2$	R20
$C_2H_5O_2 + NO \rightarrow C_2H_5O + NO_2$	R21
$CH_2COH + O_2 \rightarrow HCHO + CO + OH$	R22
$OH + CH_2 \rightarrow HCHO + H$	R23
$HCO + HCO \rightarrow HCHO + CO$	R24
$CH_3 + O \rightarrow HCHO + H$	R25
$CH_3 + O_2 \rightarrow HCHO + OH$	R26
$CH_3O + CH_2 \rightarrow HCHO + CH_3$	R27
$C_2H_3 + O \rightarrow C_2H_2 + OH$	R28
$C_2H_3 + OH \rightarrow CH_3CHO$	R29
$CH_3O + NO_2 \rightarrow CH_3ONO_2$	R30

$C_2H_5O + NO_2 \rightarrow C_2H_5ONO_2$	R31
$CH_3 + NO_2 \rightarrow CH_3NO_2$	R32
$C_2H_3 + N \rightarrow CH_3CN$	R33
$NO + N \rightarrow N_2 + O$	R34
$NO_2 + N \rightarrow N_2O + O$	R35
$NO + OH \rightarrow HNO_2$	R36
$NO_2 + OH \rightarrow HNO_3$	R37
$CO + O + M \rightarrow CO_2 + M$	R38

Varying the energy density affects the product distribution during plasma treatment, leading to an enhancement in the synergistic effect of the plasma and SCR in NO_x removal. An increase in the energy density up to 210 J L⁻¹ increased the concentration of NO₂ while decreasing the NO and NO_x (NO + NO₂) (as shown in [Figure 2](#)), revealing that a majority of NO in the feed is converted to NO₂ and a minor amount is converted to nitrogen-containing organic hydrocarbons. The NO₂ remained constant on increasing the energy density from 210 to 484 J L⁻¹ but NO constantly decreased. This reflected that the decrease in NO at these energy densities was due to a conversion to nitrogen-containing organic hydrocarbons since total NO_x also decreased. Further increase in the energy density above 484 J L⁻¹ not only decreased the NO but also NO₂, which meant that, at high energy densities, part of the NO₂ was also converted to nitrogen-containing organic hydrocarbons via reactions R30-R32. This behavior was in agreement with the proposed mechanism in [Table 1](#) for NO_x removal in the presence of hydrocarbons. NO₂ acts as an intermediate to form nitrogen-containing organic hydrocarbons from NO and high energy densities favor their formation. These species are active in the SCR [18,19]. The two-stage plasma SCR experiments using He balance instead of N₂ balance at different energy densities demonstrated that the amount of nitrogen-containing organic compounds produced following the plasma treatment was related to the N₂ and N₂O formed in the subsequent SCR process although the selectivity to N₂ remained constant at 82% [19].

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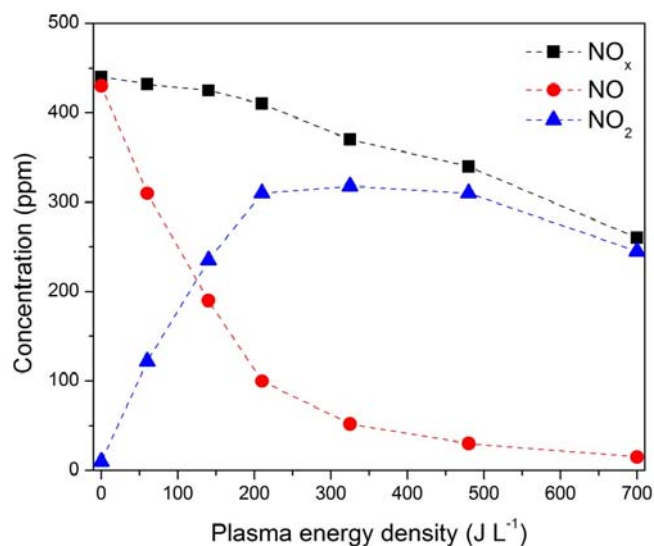


Figure 2. NO, NO₂, NO_x concentrations after plasma treatment as a function of energy density.

Adapted from [18].

Mechanistic studies of thermal C₃H₆-SCR of NO over Ag/Al₂O₃ with the assistance of a NTP using *in-situ* diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) revealed two subsequent steps in the hydrocarbon-SCR reaction: (a) nitration to generate isocyanate (-NCO) species, (b) reduction of the adsorbed NO_x species to N₂ using isocyanate, e.g. -NCO + -NO₃⁻ → N₂ + CO₂, in agreement with [18], showing that the nitrogen-containing species can improve the de-NO_x efficiency. Although NO oxidation and formation of nitrates on the catalyst surface were found to be kinetically irrelevant for the SCR reaction, the abundance of electron-rich organic species was key for the nitration process and improvement of the NO_x reduction. The Ag/Al₂O₃ catalyst was not very effective to oxidize propene (C₃H₆) and form electron-rich organic oxygenates at low temperatures (<400 °C). However, the NTP could promote the nitration step by formation of electron-rich organic oxygenates and nitrogen-contained organic species in O-predominant and N-predominant environments, respectively. The nitration step may have occurred through the reaction between

adsorbed nitrates and electron-rich organic oxygenates and also oxidation or decomposition of nitrogen-contained organic species [20].

A two-stage plasma-catalyst system placing the plasma downstream of catalytic bed has also been examined. Such hybrid sysem was reported to remove up to 30% of NO_x and almost all particulate matters (PMs) and CO from the exhaust of a light duty IDI diesel engine (2500 cc) during a dynamometer test bed and chassis dynamometer with CVS-75. A Pt-based oxidation catalyst placed in the engine exhaust was shown to oxidize almost all CO and ~50% of NO to NO₂ depending on the catalyst temperature and NO concentrations, while the plasma reactor located in the downstream of the catalyst bed, reduced NO₂ using carbonaceous particles deposited in the corona discharge reactor. The DC corona discharge is believed to have promoted the deposition of PMs and soots by electrostatic force in the plasma reactor [21].

HC-SCR was investigated by Niu *et al.* [22] over a Co-HZSM-5 catalyst with C₂H₂, C₂H₄ or CH₄ as reductants. NO conversion of 93% was obtained when using 500 ppm NO, 500 ppm C₂H₂, 15% O₂ in N₂ at 300 °C and 138 J L⁻¹ energy density. A volcano curve was obtained with further increase in temperature, as shown in [Figure 3](#). The reaction was also carried out over quartz pellets, showing <5% conversion, while the catalyst without discharge gave 80% conversion. A stronger promotion of the in plasma catalytic system compared with the thermally activated catalyst was obtained at lower reaction temperatures, with an over a 2-fold increase found below 200 °C (20% to 50%) and no NO_x removal in the plasma gas phase. However, some N₂O formation was observed under plasma conditions. Furthermore, the hydrocarbon conversion to CO_x increased from ~10% to > 80% when using the in plasma catalytic system, with CO₂/CO ratio just over 1. A similar promotion effect was obtained with C₂H₄ as reductant; however, a drop in NO_x conversion occurred at higher temperatures for the in plasma catalysis which is attributed to an increase in the rate of NO_x formation with temperature. However, the increase in CO₂/CO ratio from 6.6 to 11.7 for the plasma system compared with the thermal process may be an indication of the strong competition between the SCR activity and the full oxidation reaction of the hydrocarbon. For CH₄-SCR, the conversion increased

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only slightly from 25%-30% with the increase in temperature, while the catalyst alone showed no conversion up to 300 °C, and a maximum of 15% at 400 °C. No CH₄ conversion was observed below 300 °C and the addition of the catalyst in the discharge zone did not show a significant improvement in the NO_x conversion below 200 °C. Therefore the NO_x conversion at low temperature was proposed to be due to gas phase plasma decomposition rather than selective catalytic reduction by methane. This was further confirmed by varying the oxygen concentration in the feed with a maximum of 50% NO_x removal with CH₄ observed at 250 °C and 144 J L⁻¹ in the absence of oxygen and further decreased with an increase in oxygen.

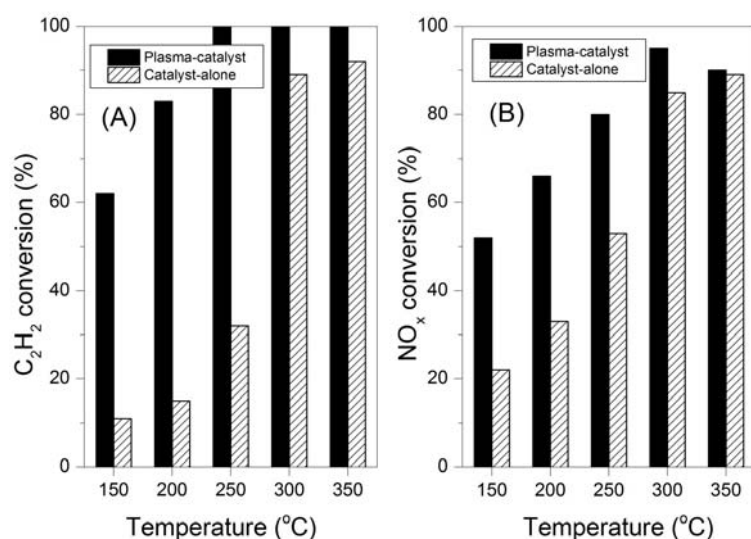


Figure 3. (A) Hydrocarbon conversion and (B) NO_x conversion as functions of temperature over Co-HZSM-5 catalyst alone and discharge over Co-HZSM-5 catalyst (500 ppm NO_x, 15% O₂, N₂ as balance gas, flow rate 520 ml min⁻¹, GHSV=12000 h⁻¹, (a) 500 ppm C₂H₂, E_{in} (150–250 °C) = 144 J L⁻¹, E_{in} (300–350 °C) = 138 J L⁻¹). Adapted from [22].

Efficient SCR of NO_x was also reported for a 12% CuO/15% TiO₂/γAl₂O₃ catalyst in a He plasma with 2% NO, 4% CH₄ and 5% O₂. A maximum of 61.4% NO_x conversion and ~ 90% CH₄ conversion

at 450 °C, was obtained with little N₂O formation and good selectivity towards N₂ [23]. Partial oxidation of CH₄ was also observed under these reaction conditions and the CO formation was observed to increase with a decrease in temperature from ~ 30% at 450 °C to almost 80% at 100 °C. Once again, removal of oxygen from the system led to an increase in the NO_x conversion to 100% through plasma dissociation since only a small CH₄ conversion (~10%) was observed under these conditions. In comparison, in the absence of the discharge the catalytic activity for NO_x removal was only 17% and ~27% with addition of O₂. The power supply was operated in a DC mode and the power consumption was 30 W. Therein, a small decrease in the specific surface area of the catalyst after reaction was reported as well as an increase in the Cu⁺ and Cu⁰ concentration after plasma discharge. It was postulated that the plasma assisted reaction could enhance the production of Cu⁺ and Cu⁰ and, therefore, the CH₄ and NO conversion since Cu⁺ is thought to be the active species at low temperature and Cu⁰ at high temperature. The reduction in oxidation state of the Cu was attributed to the formation of CO during the discharge.

Perovskite-type catalysts have also been studied in the plasma-assisted SCR of NO_x. Hueso *et al.* [5] examined the effects of the plasma-catalyst system for CH₄-SCR at low temperatures using a La_{0.5}Sr_{0.5}CoO_{3-δ} perovskite. The utilisation of a surfatron device connected to a microwave power supply at a power of 75 W and gas pressure of 4 Torr. Optical emission spectroscopy (OES) was used to characterise the plasma species and to obtain information on the changes occurring on the surface of the catalyst exposed to the discharge. X-ray photoelectron spectroscopy was undertaken following *in-situ* plasma experiments performed in a prep-chamber. In order to understand if the role of the catalyst is purely to favour the combination of the active species formed in plasma on its surface or if it actively participates in the reaction, a commercial SiO₂ powder with a high surface area (270 m² g⁻¹) was used for comparison. Under the investigated conditions, (3600 ppm CH₄, 3000 ppm NO, 3 x 10⁴ ppm O₂ in Ar or N₂ as balance gas) a decomposition yield of 97-99% for CH₄ and 88% or 68% for NO in Ar or N₂, respectively, were observed for the plasma-only reactions. N₂, O₂, H₂O and CO were the main products and less than 10% CO₂ formation was observed. The synergetic effect of the plasma and catalyst was identified for a simplified mixture containing only CH₄ and O₂. The results

showed a dramatic increase in the CO₂ selectivity, with a temperature dependant conversion-efficiency, showing a maximum of ~ 90% both in a Ar or N₂ plasma at 190 °C. This behavior was only observed when La_{0.5}Sr_{0.5}CoO_{3-d} was used as catalyst, and it was postulated that the perovskite directly participated in the oxidation of CO to CO₂. A simpler role of providing surface reaction sites at which active plasma species (CO*, OH*, CH*, H*, O* for Ar plasma or N₂*, CN*, NO* for N₂ plasma) react with each other, as would be the case when using SiO₂ was discarded.

The synergetic effect was explained through the formation of new active sites or oxygen on the surface of the catalyst which was due to the direct contact of the Reactive Oxygen Species (ROS) produced by plasma (O*, OH*) with the catalyst. The study also showed that NO addition to the feed did not have a significant impact on the CO₂ selectivity. The NO removal efficiency decreased when the catalyst was placed in the discharge zone, in particular with N₂ as balance gas. The results were attributed to the NO formation by the interaction between the excited NO* and other N-containing species formed by the plasma and the oxide ions of the catalyst surface, giving rise to the –NO_x and –NO₂ species that were identified in the XPS spectra.

The interaction of the ROS produced by the plasma with the surface of the catalyst is very important as it can have a beneficial effect in removing species that can, otherwise, easily accumulate on the catalysts at low temperature reaction conditions leading to deactivation of the catalysts. One such example can be found in the work of Stere *et al.* who studied the selective catalytic reduction of NO_x with octane or toluene over a 2% Ag/Al₂O₃ using a DBD reactor and an *in situ* DRIFTS-MS system [24,25]. The results shown in [Table 2](#) demonstrated that the SCR activity was strongly enhanced by the presence of the catalyst in the discharge area ([Figure 4](#)) for a mixture containing 720 ppm NO, 4340 ppm C1, 4.3% O₂, 7.2% H₂O and 7.2% CO₂ with a balance of helium balance. Up to 50% NO_x reduction was observed for the hybrid plasma catalyst system at ambient temperature conditions with the catalyst in the discharge area, while without the catalyst, a decrease in conversion to 11.5% was obtained when octane was used as a reductant and to 4% with toluene. A decrease in the reduction of NO_x with the reaction temperature (250 °C) for the octane-SCR

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highlighted the competitive reactions occurring in this process, *i.e.* the partial oxidation of the hydrocarbon (leading to N_2 production by NO reduction) and the complete oxidation of the octane (thus, reduced NO_x conversion), and the need to fine tune the reaction parameters. At low temperatures the partial oxidation was favoured leading to NO_x conversion whereas at higher temperatures, the octane was completely combusted and limited the NO_x conversion. Interestingly, it was reported that, when using toluene, an increase in temperature led to an increase in NO_x conversion. This was attributed to the fact that toluene is less easily oxidised compared with octane and, therefore, partial oxidation occur over a wider temperature windows. Another benefit of the IPC system was a decrease in the rate of deactivation compared with the thermal system while maintaining good N_2 selectivity and low N_2O formation.

Table 2. NO_x and Hydrocarbon Conversion (Conv) and Selectivity to N₂, N₂O, CO, and CO₂ during the Toluene-SCR of ¹⁵NO in the Presence of the NTP
Using the Blank Reactor, the Reactor in the Presence of the Thermocouple, and the Reactor in the Presence of the Thermocouple and 2% Ag/Al₂O₃ Catalyst
at Ambient Temperature. Adapted from [24].

Experiment	NO _x				C ₇ H ₈			
	Total NO _x Conv (%)	N ₂ (%)	N ₂ O (%)	Unknown (%)	HC Conv (%)	CO (%)	CO ₂ (%)	Unknown (%)
Empty reactor	4.0	Trace	Trace	N/A	7.5	Trace	Trace	N/A
Blank reactor + thermocouple	24.5	75.9	2.2	21.9	71.9	13.2	73.8	13.0
2% Ag/Al ₂ O ₃ in the presence of a thermocouple	42.4	96.1	1.5	2.3	89.1	10.6	90.0	N/A
Experiment	NO _x				<i>n</i> -C ₈ H ₁₈			
	Total NO _x Conv (%)	N ₂ (%)	N ₂ O (%)	Unknown (%)	HC Conv (%)	CO (%)	CO ₂ (%)	Unknown (%)
Empty reactor	11.5	Trace	Trace	N/A	4.5	Trace	N/A	N/A
Blank reactor + thermocouple	34.8	75.9	23.8	0.3	79.2	9.2	90.1	0.7
2% Ag/Al ₂ O ₃ in the presence of a thermocouple	51.7	77.9	21.5	0.6	98.8	13.5	86.1	0.4

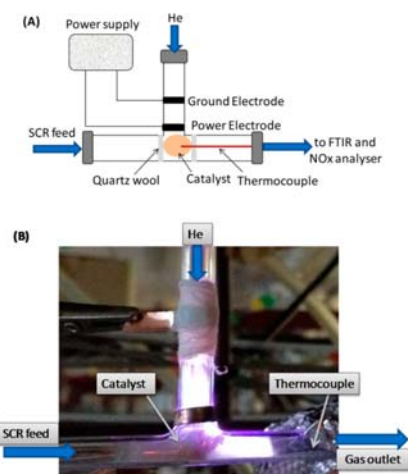


Figure 4. Schematic (A) and photograph (B) of the plasma reactor used during the HC-SCR activity test. Reprinted with permission from [24]. Copyright 2014 American Chemical Society.

The remarkable enhancement in conversion and N_2 selectivity was further investigated using a combined DRIFTS hybrid plasma system. The *in-situ* mechanistic study was performed using a state of the art cell (Figure 5) [25] designed to allow the interaction of the plasma stream with the surface of the catalyst bed, on which infrared spectra were simultaneously collected.

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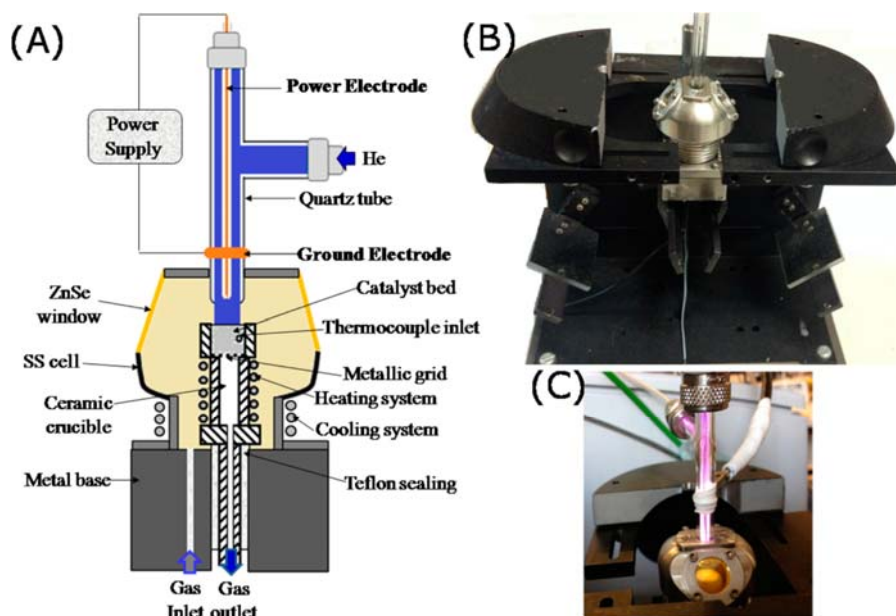


Figure 5. DRIFTS-MS setup: (A) schematic sketch of the modified dome for the NTP-DRIFTS-MS measurements; photograph of the (B) setup and (C) the metallic dome with plasma on. Reprinted with permission from [25]. Copyright 2014 American Chemical Society.

The *in-situ* IR measurements provided invaluable information on the adsorbed species in the presence of plasma leading to more insights on the mechanisms of the reaction for the plasma-assisted SCR with octane and toluene. It was postulated that the NTP might play an important role in cleaning the surface of the catalyst, since the deactivation of the plasma-SCR reaction was not as prevalent as in the case of thermally activated process. Furthermore, the formation and disappearance of IR bands associated to isocyanate and cyanide species -NCO/-CN , gave valuable information on the reaction mechanism for the plasma assisted-SCR. It is believed that under the investigated conditions, the octane-SCR reaction proceeded through a similar reaction mechanism to the thermal case, with the isocyanate species observed at 2260 cm^{-1} being a key intermediate in the NO_x removal mechanism, formed via R-NO_2 compounds as well as from the conversion of cyanide species [26]. Interestingly, for the toluene it was suggested that both the R-ONO and the R-NO_2 routes might be occurring or

only the R-ONO route, given that no -NCO was detected, while the band at 2165 cm^{-1} , attributed to cyanides, increased under plasma reaction.

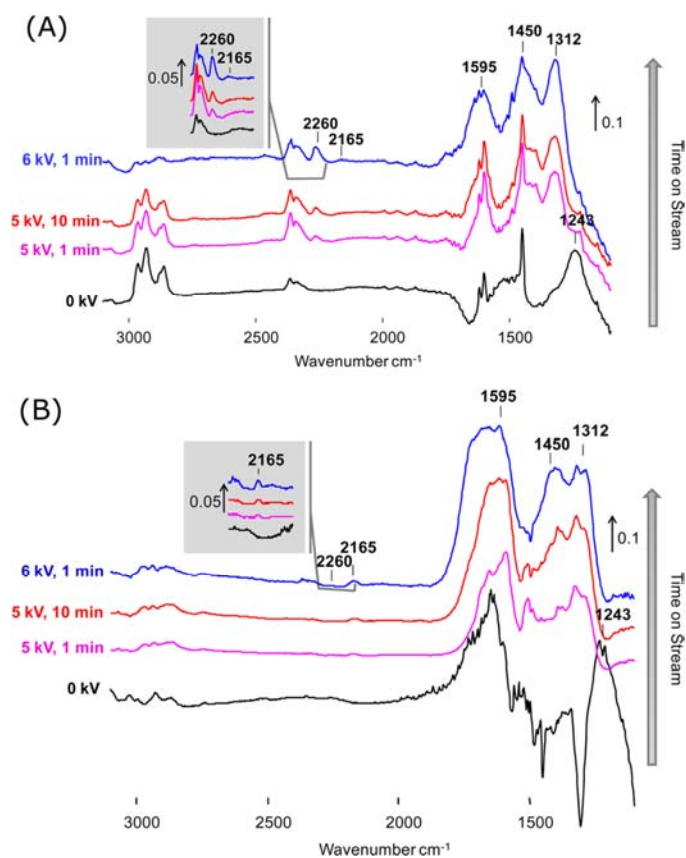


Figure 6. Changes in surface species observed during the (A) n-octane-SCR and (B) toluene-SCR of NO_x over 2 wt % $\text{Ag}/\text{Al}_2\text{O}_3$ with and without plasma. Feed composition: 720 ppm of NO , 540 ppm of $n\text{-C}_8\text{H}_{18}$ or 620 ppm of C_8H_{18} equivalent of 4340 ppm as C1, 4.3% of O_2 , and He balance. The total flow rate was $100\text{ cm}^3\text{ min}^{-1}$. Reprinted with permission from [25]. Copyright 2014 American Chemical Society.

In summary, the plasma-catalyst system was shown to have a synergistic effect on HC-SCR process and increased the NO_x removal efficiency. The promotion effect of plasma-catalyst system is more pronounced at low temperatures (< 300°C), where the catalyst-alone is not active. Formation of oxygenated species such as aldehydes and nitrogen-contained organic compounds and conversion NO to NO₂ during plasma are reported as the reasons for higher de-NO_x efficiency in plasma-catalyst system.

3. NH₃-SCR using NTP

The NH₃-SCR system is a mature de-NO_x technology which has been widely used to remove NO_x from stationary flue gases since 1980s and has been extended to automotive application more recently. Several investigations have demonstrated that NO_x conversion rate increases at low temperatures (< 250°C) with an increase in NO₂/NO ratio especially if an equimolar ratio of NO and NO₂ in the exhaust is achieved [11,27] *i.e.* the reaction (2) has a higher rate at low temperatures, compared to reaction (1).



In keeping with this approach pre-oxidation of NO to NO₂ using NTP generated by a DBD reactor upstream of a NH₃-SCR reactor was reported to improve the de-NO_x efficiency in the 100 - 250 °C range [27]. The results of treating the filtered exhaust of a 4.4 kW diesel generator, containing NO, NO₂, hydrocarbons, CO, aldehydes and O₂, with a two-stage plasma-NH₃-SCR reactor using a V₂O₅/TiO₂ monolithic catalyst is shown in [Figure 7](#). The NO and NO₂ concentration profiles obtained after the plasma reactor evidence the conversion of NO to NO₂ with increased energy density, an concurrent increase in NO_x removal efficiency obtained after two-stage plasma-NH₃-SCR at 100 °C. At about 60 J L⁻¹, which corresponds to almost equal NO and NO₂ concentrations, the NO_x removal efficiency is relatively high and with further increases in the energy density, the NO_x removal efficiency stabilizes [11].

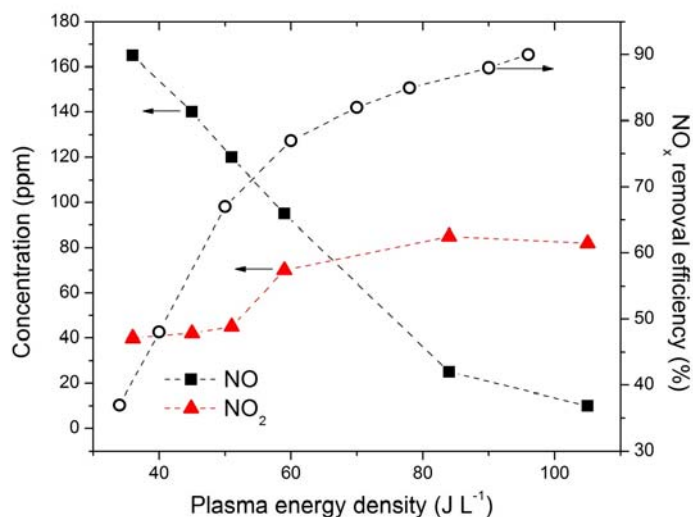


Figure 7. Effect of specific energy density on NO and NO₂ concentrations at the exit of plasma reactor and on NO_x removal efficiency during two-stage plasma-NH₃-SCR system. Adapted from [11].

Wang *et al.* [28] examined the efficiency of plasma-assisted catalytic system for NO removal using a 4 wt.%Cu 4 wt.%Ce/ZSM-5 catalyst in the presence of 500 ppm NO, 500 ppm NH₃, 6% O₂ in N₂ and a 60000 h⁻¹ GHSV. Therein, up to 90.7% and 80.1% NO and NO_x, respectively, removal efficiencies were achieved at 180 °C and an energy density of 367 J L⁻¹. In the absence of a catalyst, the removal efficiencies were 34% and 12% for NO and NO₂, respectively. It was postulated that the oxidation of NO was facilitated by the increased oxygen migration between Cu and Ce and Cu ions could be incorporated into the vacant sites on the CeO_x surface to form oxygen vacancies, which increased the amount of adsorbed oxygen species on the surface of the catalyst. The increased catalytic reduction of NO at ambient temperature was attributed to the low thermal stability of the acid sites of the 4 wt.%Cu 4 wt.%Ce catalyst.

The addition of propene to the feed and an increase in input voltage enhanced the de-NO_x efficiency of the plasma-NH₃-SCR system. However, these changes also generated a significant amount of by-

products such as CO, N₂O, HCHO, CH₃CHO at the outlet of SCR reactor [27]. Previous work reported a synergistic effect in NO_x removal efficiency using a hybrid plasma-catalyst system using a NH₄⁺ modified zeolites as the SCR catalyst in a DBD reactor in the presence of high oxygen concentrations at 100 °C. As found for the HC-SCR reaction, it is believed that plasma converts some NO to NO₂ which ultimately leads to an increase of the NO_x removal efficiency [29].

4. NO_x storage-reduction catalysis (NSR) using NTP

NO_x storage-reduction technology (or lean NO_x trap (LNT)), first introduced by Toyota, is used commercially to remove the NO_x emissions from the exhaust of light-duty diesel vehicles. This technology works using fuel-lean and fuel-rich cyclic conditions wherein the fuel-lean condition (excess O₂) leads to the NSR catalyst adsorbing NO_x. Thereafter, during the fuel-rich condition (excess reductant) the adsorbed NO_x reduces to N₂. The NSR catalyst requires sites for adsorption of NO_x and also sites for the reduction of NO_x. Pt/BaO/Al₂O₃ is the most common catalyst for NSR catalysis and has a good performance at temperature above 300°C. Due to low exhaust gas temperatures (180 - 350°C) of light-duty diesel vehicles, low temperature NSR catalysts are required [30]. Therefore, as an attempt to address the low temperature NO_x removal efficiency non-thermal plasma-catalyst system had been tested.

A number of research studies developed a DBD reactor and applied NTP to the rich phase of the NSR process (IPC system) using different catalysts including a perovskite catalyst (LaMn_{0.9}Fe_{0.1}O₃) [30] and M/BaO/Al₂O₃ formulations with M = Mn, Fe, Co, Ni, Cu, Pt [31,32]. In comparison to a Pt/BaO/Al₂O₃ catalyst, the Pt-free catalysts exhibited higher NO_x storage capacity, in the fuel-lean feed containing NO, O₂ and an Ar balance at low temperatures (30 – 300 °C) but also significantly lower activity in NO_x removal step under fuel-rich conditions containing H₂ and an Ar balance. The low activity of these catalysts in the NO_x reduction step was significantly improved by the use of the NTP, attributed to the facile H₂ activation during NTP (Table 3). For example, high NO_x conversions (up to 90%) between 150-350 °C using Co/Ba/Al₂O₃ was reported [32]. The effect of CO

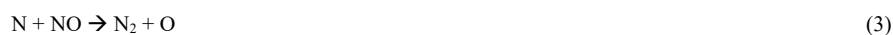
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versus H₂ as the reductant during plasma-NSR over Pt/Ba/Al₂O₃, Pd/Ba/Al₂O₃ and Pd/Co/Ba/Al₂O₃ was also investigated. The addition of CO reduced the NO_x conversion significantly at low temperatures over both Pt/Ba/Al₂O₃ and Pd/Ba/Al₂O₃. In contrast, the Pd/Co/Ba/Al₂O₃ was shown to have a better activity in the presence of CO in the plasma-NSR process with NO_x conversions close to 99% at 150-350 °C [33]. These studies did not investigate the effect having small amount of O₂ in the rich phase or the use of N₂ as balance gas instead of Ar balance, which was known to significantly change the results during NTP.

Table 3. NO_x storage capacity measured at lean conditions (500 ppm NO, 8% O₂ and Ar balance; GHSV = 14,400 mL g_{cat}⁻¹ h⁻¹; time = 50 min); NO_x conversion during storage and reduction experiment (lean phase: 500 ppm NO, 8% O₂ and Ar balance, time = 10 min; rich phase: 2% H₂ and Ar balance, time = 2 min); NO_x conversion during plasma-assisted storage and reduction experiment (lean phase: 500 ppm NO, 8% O₂ and Ar balance, time = 10 min; rich phase: power = 1.8 w, 2% H₂ and Ar balance, time = 2 min) over different catalysts as a function of temperature. Adapted from [31].

Catalyst	NO _x storage capacity		NO _x conversion (%)			
	(μmol g ⁻¹)		NSR		NTP-NSR	
	200	350	200	350	200	350
Pt/Ba/Al ₂ O ₃	175	248	38	89	71	98
Co/Ba/Al ₂ O ₃	260	265	16	10	100	100
Ni/Ba/Al ₂ O ₃	210	265	8	47	97	90
Mn/Ba/Al ₂ O ₃	264	265	20	26	100	100
Cu/Ba/Al ₂ O ₃	205	265	4	26	55	100
Fe/Ba/Al ₂ O ₃	120	170	5	28	78	100

Wang *et al.* [34,35] similarly combined NTP with NO_x storage and reduction or decomposition over a H-ZSM-5 (Si/Al = 22) catalyst (IPC system). In this study, the NO_x containing feed was adsorbed on the catalyst for a long time at room temperature before the stored NO_x was reduced to N₂, N₂O. The reduction was performed under oxygen lean conditions (e.g. 5% O₂ and 95% N₂) using NTP and a reductant (CH₄ and NH₃) at room temperature for a short period of time. The NO_x desorption and conversion to N₂ were correlated with the energy density of the plasma and the concentration of the reductant (maximum NO_x conversion to N₂ was 95%). N₂O was found to be the main by-product during this process and its decomposition to N₂ and O₂ was facilitated by an increase in the plasma energy density. Both CH₄ and NH₃ as reducing agents were shown to be very effective in controlling the NO_x. In addition to the NSR process, NO decomposition in plasma under oxygen lean condition has been shown to occur in the absence of a reductant through:



However, the extent to which this reaction occurred was limited due to the lower dissociation energy of O₂ compared to N₂. In the presence of NH₃, NH_x based free radical species were formed which reduced NO to N₂ through:



increased the NO_x removal efficiency due to activation of NH₃ being easier compared with N₂ [34]. CH₄ is believed to not only act as a reducing agent but also limit the reverse reaction, i.e. formation of NO_x, by consuming oxygen. An increase in CH₄/O₂ ratio resulted in an increase in NO_x conversion up to 95% and CH₄ was found to be completely converted to CO₂ during the plasma-NSR process [35].

The addition of 2% H₂O and 2% CO₂ to the feed in the plasma-NSR process over Co/Ba/Al₂O₃ catalyst was found to significantly inhibit the NO_x reduction efficiency and remove the benefits of NTP. This effect was attributed to a decrease in the NO_x storage capacity of the Co/Ba/Al₂O₃ catalyst in the presence of H₂O and CO₂. The addition of Pd to the Co/Ba/Al₂O₃ catalyst mitigated the inhibition effect of H₂O and CO₂ in the plasma-NSR system and increased the stability of that catalyst both with and without the presence of H₂O and CO₂ [32]. Similar results were obtained on the

addition of 2% H₂O to the feed during plasma-facilitated NO_x storage and decomposition or reduction using CH₄ over a H-ZSM-5 catalyst. Therein, the NO_x conversion and selectivity to N₂ were decreased; however, H₂O did not have any effect on the process using NH₃ as the reductant [34,36]. H₂O was shown to compete with NO_x during storage step, promote formation of N₂O in the reduction step and thus, decrease NO_x reduction efficiency [36].

In another approach NTP was applied to the lean step of the NSR process (storage step). Li *et al.* [37] reported an enhancement in NO_x storage capacity of a Pt/Ba/Al₂O₃ catalyst at 100 - 300°C when using a plasma-catalyst system compared with the thermally activated process. In this case, the plasma increased the NO to NO₂ oxidation rate via O-radicals formed by collision of electrons with O₂ in the gas phase. NO_x storage capacity could be further increased by having the catalyst in plasma discharge zone rather than the plasma followed by the catalyst bed. The catalyst in the plasma discharge zone not only adsorbed the NO₂ formed by plasma but also adsorbed the NO from the gas-phase which then reacted with adsorbed oxygen radicals and forms more NO₂ which then contributed to higher NO_x storage capacity [37].

5. NO oxidation using NTP-catalyst system

As noted for the NSR catalysis, whilst NO is the dominant species in the exhaust, it adsorbs weakly on the catalyst surface and thus, it is common to first convert NO to NO₂ which can improve the catalytic activity in the NO_x reduction process at low temperatures (although some research studies have questioned the role of NO oxidation in NO_x removal especially in the presence of hydrocarbons) [18,19,38]. In applications associated to the stationary sources *e.g.* waste gas streams, it is proposed to extend the oxidation of NO further to N₂O₅, which can be easily removed by various air pollution control systems such as wet or semi-dry scrubbers. There is a patented process called low-temperature NO_x (LoTOx system), in which ozone injects to the exhaust stream to convert NO to NO₂ and further to N₂O₅ [39–42]. This process was shown to remove 90% of NO_x emissions [39]. Jogi *et al.* [43] investigated NO oxidation using a hybrid plasma-catalytic reactor (IPC system; fed by a mixture of

NO, O₂ and N₂) and an ozone injector (air plasma or O₂ pure plasma) followed by a fixed-bed catalytic reactor (PPC system; fed by ozone, NO and N₂) at 10-500 J L⁻¹ using Fe₂O₃ and TiO₂ as catalysts. The hybrid plasma-catalytic reactor was not efficient for NO removal e.g. the 450 ppm inlet NO concentration decreased by 40-50 ppm in the outlet when increasing the plasma energy density up to ~230 J L⁻¹ and only NO₂ was observed as product. In contrast, the ozone injection reactor was able to oxidize all NO to NO₂ at 10-12 J L⁻¹ and further to N₂O₅ by an increase in plasma energy density, correlated to the O₃ concentration. The catalyst presence in the ozone injection reactor contributed not only to O₃ destruction, so that the outlet O₃ concentration significantly decreased, but also to further NO oxidation to N₂O₅ [43].

The effect of catalyst placement in the discharge zone during NO oxidation in the hybrid plasma-catalytic reactor was also tested. Both configurations (catalyst placed at the outlet or along the full-length of the discharge zone) led to an improvement in the NO to NO₂ oxidation, compared with in the absence of the catalyst or when the catalyst was placed at the inlet of discharge zone. Without the catalyst, NO was oxidized to NO₂ in the discharge zone and on increasing the NO₂ concentration in the bed, the reverse reaction occurred until the reaction reached equilibrium. If the catalyst was placed in the inlet of discharge zone, the NO₂ formed via the catalyst was converted back to NO by the end of the reactor where no catalyst was present [44].

The ozone injection reactor (with TiO₂ as the catalyst) was further studied at different catalyst temperatures, flow rates and inlet NO concentrations [42]. NO to NO₂ oxidation was correlated with the inlet O₃ concentration. When inlet O₃ concentration reached the NO concentration at inlet condition, all NO was oxidized to NO₂. Further increases in the inlet O₃ concentration led to further oxidation of the NO₂ to N₂O₅ (Figure 8). ~~Figure 8~~

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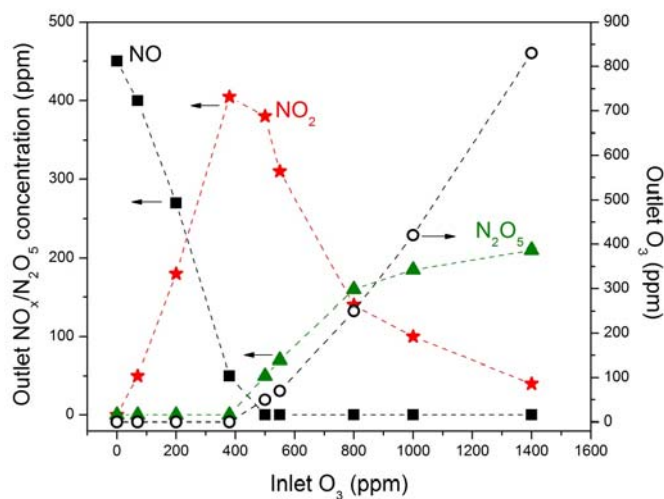


Figure 8. Effect of inlet O₃ concentration on the outlet concentrations of NO, NO₂, O₃ and N₂O₅ at 20°C in ozone injection reactor with TiO₂ as the catalyst. Adapted from [42].

The TiO₂ catalyst did not have any detectable effect on the reaction at low temperatures but improved the conversion of NO₂ to N₂O₅ at high temperatures. The NO₂ to N₂O₅ reaction is believed to be limited by the formation of NO₃ which can be enhanced by the catalyst. For example, NO₂ can adsorb on the catalyst surface and form NO₃ species ($\text{NO}_{2(\text{g})} + \text{O}^* \rightarrow \text{NO}_3^*$) using surface oxygen species supplied by O₃ decomposition ($\text{O}_{3(\text{g})} + * \rightarrow \text{O}_{2(\text{g})} + \text{O}^*$). Thereafter, these species react with another NO₂ to form N₂O₅. The stoichiometric ratio of [O₃]/[NO] to convert all NO to N₂O₅ is 1.5. One way to improve the efficiency of ozone injection reactor from an industrial point of view would be to operate at stoichiometry where the lowest amount of O₃ is consumed. Jogi *et al.* [42] reported that this ratio can be reduced by the effect of several operating parameters (Figure 9). For example, an increase in the inlet [NO], an increase in temperature, a decrease in flow rate or the presence of catalyst all led to a decrease in the [O₃]/[NO] ratio.

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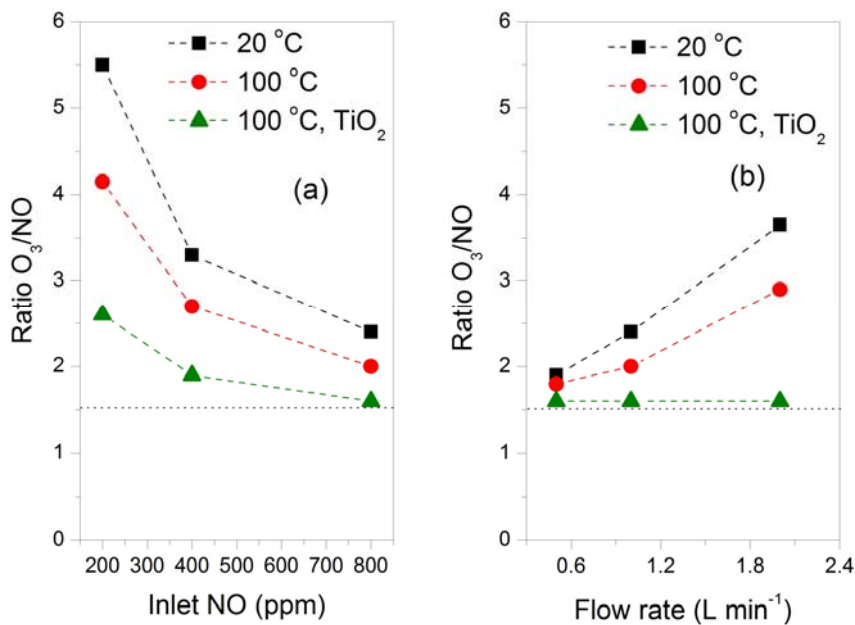


Figure 9. The ratio of inlet O_3 to inlet NO concentrations when 95% of NO is converted to N_2O_5 as a function of (a) inlet NO concentration; (b) flow rate. Adapted from [42].

6. Conclusions and recommendations

The combination of NTP and catalysis has been examined in various reactor configurations to enhance the performance of the current de- NO_x technologies such as SCR and NSR applicable to the exhaust gas streams of stationary or mobile sources under lean conditions. Technically, the plasma-catalyst system has been shown to have a synergistic effect on the de- NO_x efficiency. The plasma-catalyst system is mostly applied at low temperatures ($< 300^\circ C$) where current thermally activated technologies are not efficient.

Predominantly, NTP has been combined with SCR in a two-stage system configuration, where a flow of feed is first passed through the NTP and, thereafter, the outlet gases are reacted over a fixed bed

catalytic reactor. In general, the NTP leads to the formation of oxygenated species such as aldehydes, nitrogen-containing organic species and NO is converted to NO₂, which improve the reduction efficiency to N₂ during the HC-SCR reaction. An increase in plasma energy density was correlated to having higher de-NO_x efficiency. Furthermore, NTP has been used as a pretreatment to convert the NO to NO₂ before NH₃-SCR reactor, which is believed to improve the NO_x reduction efficiency at low temperatures.

The NTP has been applied to the NSR using different concepts. In one case, it is applied to the lean phase of the NSR and expected to improve the adsorption capacity of the catalyst by conversion of NO to NO₂. Alternatively, a catalyst with high adsorption capacity is chosen and the NTP is applied to the rich phase to improve the reduction activity of the catalyst at low temperature. Both were shown to be successful, although for most of the catalysts studied, inhibition by addition of H₂O and CO₂ to the feed was observed.

Finally, NO oxidation has been studied to improve the NO_x removal processes using plasma-catalyst system in different reactor configurations relevant to both mobile and stationary sources' applications. Although an increase in plasma energy density generates more O₃ which converts NO to NO₂ and finally to N₂O₅, the catalyst is shown to destruct the O₃ residuals and contribute to the efficiency of N₂O₅, which is attributed to the facile of formation of NO₃ species on the catalyst surface.

While not so many studies have been focusing so far on the in-plasma configuration, placing the catalyst in the discharge zone could open new routes towards efficient NO_x removal but there are still significant challenges to overcome as finding the suitable materials, reactor design and operation conditions, including gas composition and discharge type [45,46] can be the game changing parameters.

Despite of the many investigation reported on NO_x removal using plasma-catalyst system and claim of synergistic effect, there is no report of demonstration of this system on a vehicle. However, a pilot

scale aftertreatment system that was a combination of NTP and adsorption has been designed and successfully met the most recent International Maritime Organization NO_x emissions standards by removing 94% of NO_x in the exhaust of a marine diesel engine [47,48]. This system operated on adsorption and desorption cycles where plasma was on during desorption cycle only and required ~4% of output engine power.

Despite commercial applications of NTP in the wastewater treatments, air pollution control or food and beverage industries [49,50], one of the challenges in commercial use of plasma-based systems in emission control is energy requirements to drive NTP if used continuously. In the investigations covered by the present review, the energy density required to decrease emissions in the exhaust ranged from 10 to almost 2000 J L⁻¹. This corresponds to less than 1 BHP per liter of the engine intermediate load for the lower range while the higher end corresponds to several tens of BHP per liter which is unlikely to be acceptable. It is therefore clear that the energy requirement of such plasma-based systems will need to be at the heart of their development to be viable future solutions. Some proposed ways to reduce energy requirements associated with the NTP-catalyst systems are the development of novel catalysts, optimizing the power supply and operation mode and also design of reactors suitable for each particular application. The energy requirement can be managed if the NTP is not used continuously. As described earlier, a NTP-based aftertreatment system for marine diesel was successfully optimized using cyclic operation where plasma was only on in desorption cycles and for a short time.

Catalysts designed for NTP operation also present an opportunity to improve the energy load. These should be optimised to enhance the synergy of combining the catalyst with the NTP discharge zone. Therefore, the dielectric constant, pore size, acidity of the materials become important parameters to consider for these applications, as already discussed by various groups [46,51–55]. Although there is an enhancement in the de-NO_x efficiency observed when using a plasma-catalyst system, high energy densities are required to activate the catalysts in the plasma at low temperatures. Mechanistic studies using thermal characterization methods to understand the surface changes, kinetics and reaction

elemetry steps occurring on the catalyst surface can be helpful towards designing novel catalysts. For example, plasma treatment was shown to affect the acidity of zeolite catalysts [55]. Liu *et al.* [56] observed an increase in Lewis and Brönsted acidity of Pd/HZSM-5 catalyst when pre-treated in glow discharge plasma, followed by air-calcination, leading to an increase in Pd dispersion and thus, an enhancement in catalytic activity and stability during methane oxidation. Acid zeolite or ion exchanged zeolite catalysts are currently the preferred choice for the SCR reaction. Kwak *et al.* [57] reported an increase in NO_x conversion by an increase in the acid sites of H⁺ modified NaY zeolites during plasma-assisted SCR of a simulated diesel engine exhaust gas mixture. Considering the plasma effect on catalyst acidity of zeolites, this creates an opportunity to develop new improved catalyst for NO_x removal using plasma-assisted catalyst systems.

The other possible way to reduce energy requirements is to design a plasma-catalyst reactor with higher energy efficiencies that should be also compatible with the exhaust system. Most of studies in the literature used DBD reactor with two reactor configurations (IPC and PPC) for NO_x removal as extensively studied in this paper. There are limited studies combined other types of plasma reactors such as gliding arc, radio frequency, microwave discharge and corona discharge with catalyst for NO_x removal. Indarto *et al.* [58], investigating the decomposition of CO₂ using gliding arc reactor, claimed that the gliding arc reactor had better energy efficiency compared to DBD, corona discharge and radio frequency plasma systems. Kim *et al.* reported NO_x reduction over γ -Al₂O₃, mechanically mixing γ -Al₂O₃ with TiO₂ and BaTiO₃ and Co-ZSM-5 catalysts using a combined pulse corona discharge with catalyst system in both IPC and PPC reactor configurations. The highest de-NO_x efficiency was obtained using the IPC system with γ -Al₂O₃ as the catalyst and addition of a reductant (e.g. methanol). The energy densities reported are in the range of 10-160 J L⁻¹, similar to the energy densities of DBD reactors.

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